

AD-A067 671

VIRGINIA UNIV CHARLOTTESVILLE DEPT OF CHEMISTRY  
TETRACARBON METALLOCARBORANES 7. COBALT SYSTEMS DERIVED FROM (C--ETC(U)  
APR 79 W M MAXWELL, R N GRIMES

F/G 7/3

N00014-75-C-0305

NL

UNCLASSIFIED

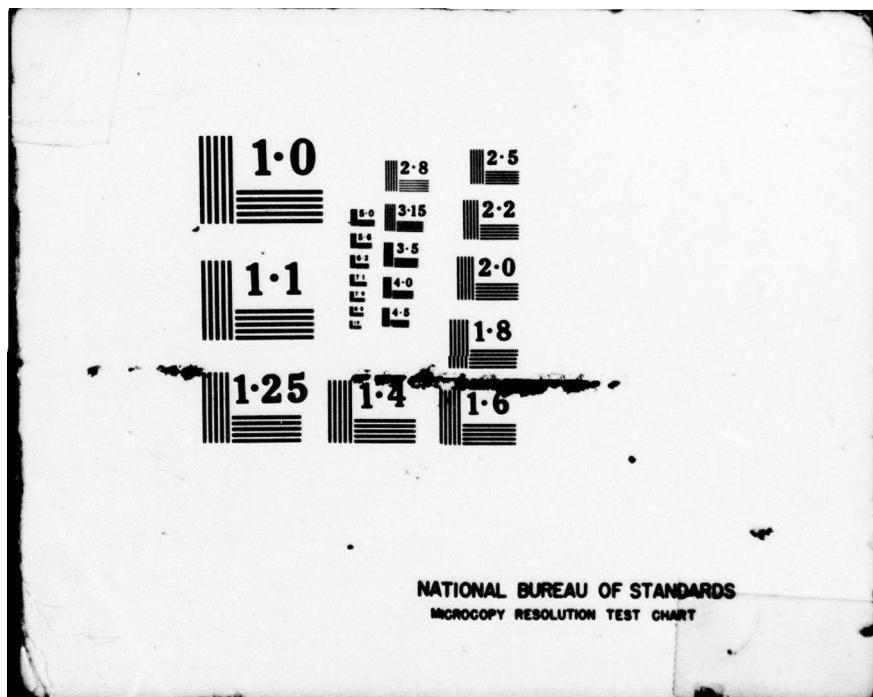
TR-28

1 OF  
ADA  
067871



END  
DATE  
FILED

© 79  
DDC



DDC FILE COPY AD A067671

12

LEVEL <sup>III</sup>

AO55002

OFFICE OF NAVAL RESEARCH

15

CONTRACT NO. NO0014-75-C-0305

Task No. NR 053-569

9

TECHNICAL REPORT NO. 28

14

TR-28

6

Tetracarbon Metallocarboranes. 7.

Cobalt Systems Derived from

$(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ . Synthesis and

Interconversion of 11-, 12-, and

13-Vertex Nido Cages.

A055 75P

10

William M. Maxwell ■ Russell N. Grimes

Department of Chemistry, University of Virginia  
Charlottesville, Virginia 22901

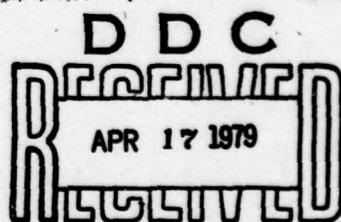
Prepared for Publication

in

Inorganic Chemistry

11

April, 1979



49

Reproduction in whole or in part is permitted  
for any purpose of the United States Government

12 30P.

Approved for public release; distribution unlimited

401 147

79 04 12 028

mt

Contribution from the Department of Chemistry  
University of Virginia, Charlottesville, VA 22901

Tetracarbon Metallocarboranes. 7. Cobalt Systems Derived from  
 $(CH_3)_4C_4B_8H_8$ . Synthesis and Interconversion of 11-, 12-, and 13-Vertex  
Nido Cages

William M. Maxwell and Russell N. Grimes\*

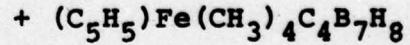
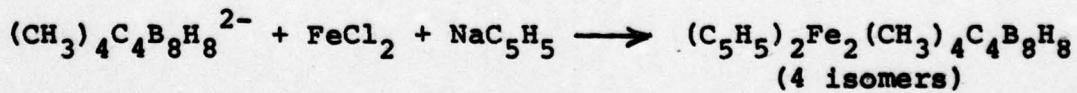
Abstract. Further studies of the novel structural chemistry that has been encountered in carbon-rich metallocarboranes are described. The preparation, isolation, and characterization of new nido-metallocarboranes containing four skeletal carbon atoms is presented, and mechanisms are proposed for their formation. The insertion of cobalt into  $(CH_3)_4C_4B_8H_8$  via reaction with  $(\eta^5-C_5H_5)Co(CO)_2$  under uv light produced  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_7H_7$ , isomer I, and  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_6H_6$ , isomers I and II. The same  $CoC_4B_7$  isomer was obtained from the closo, nido- $[(CH_3)_2C_2B_4H_4]Co[(CH_3)_2C_2B_3H_5]^-$  ion by oxidative fusion of the ligands followed by reaction with  $CoCl_2$ ,  $NaC_5H_5$ , and  $O_2$ . Treatment of the  $(CH_3)_4C_4B_8H_8^{2-}$  dianion with  $CoCl_2$ ,  $HCl$ , and  $O_2$  generated  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_7H_7$ , isomer II,  $\sigma-[(\eta^5-C_5H_5)Co(\eta^5-C_5H_4)]-(CH_3)_4C_4B_8H_8$ , and  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_8H_8$ , of which the first two products have been structurally characterized by X-ray studies. From  $^{11}B$  and  $^1H$  FT NMR, IR, and low- and high-resolution mass spectroscopic data, and from electronic, synthetic, and mechanistic considerations, structures are proposed for the remaining  $CoC_4B_6$ ,  $CoC_4B_7$ , and  $CoC_4B_8$  cage isomers. A third isomer of  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_7H_7$  was obtained on rearrangement of isomer I at  $140^\circ$ .

1.

79 04 .12 028

### Introduction

Synthetic and structural investigations of four-carbon carborane and metallocarborane cage systems have been a continuing project in our laboratory,<sup>2</sup> through which we are attempting to develop systematic relationships between skeletal electron population, molecular geometry, and mechanisms of cage formation and rearrangement. The preparative routes to tetracarbon metallocarboranes as they have developed thus far, are of two main types: fusion of dicarbon metallocarboranes to produce dimetallic four-carbon cages<sup>1,3-6</sup> (schematically,  $2 C_2 B_n M \longrightarrow C_4 B_{2n} M_2$ ), and insertion of metal groups into tetracarbon carboranes.<sup>7</sup> The second route has been employed to generate 12-, 13-, and 14-vertex metallocarboranes of iron, cobalt, nickel, molybdenum, and tungsten from neutral  $(CH_3)_4 C_4 B_8 H_8$  or its dianion, e.g.,



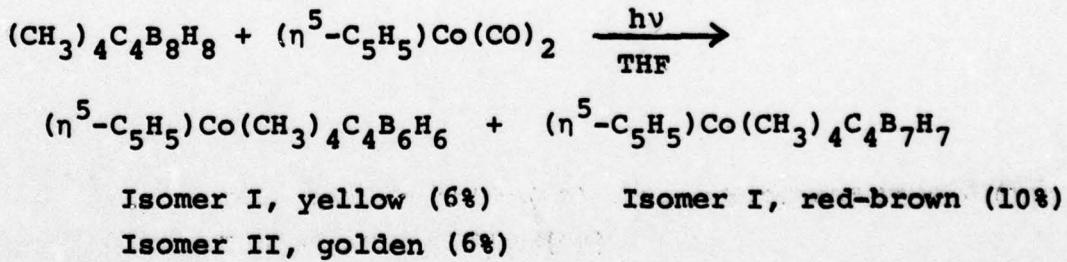
We have previously described the synthesis and rearrangements of the iron species, together with X-ray crystallographic studies of several key compounds.<sup>7,8</sup> Although one might simplistically expect the insertion of  $(n^5-C_5 H_5) Co^{2+}$  units into  $(CH_3)_4 C_4 B_8 H_8$  or its dianion to parallel that of iron and hence yield similar

DISTRIBUTION/AVAILABILITY CODES		
Dist.	AVAIL	and/or SPECIAL
A		

stereochemistry, this is not the case. The cobalt reactions, which are the subject of this paper, in fact follow a quite different course and generate a series of tetracarbon cobalta-carboranes which are structurally distinct from their iron counterparts.

## Results and Discussion

Direct Insertion of Cobalt into Neutral  $(CH_3)_4C_4B_8H_8$ . The reaction of  $(CH_3)_4C_4B_8H_8$ , a colorless, air-stable solid, with  $(\eta^5-C_5H_5)Co(CO)_2$  in tetrahydrofuran (THF) under ultraviolet light at  $27^\circ C$  produced several cobaltacarboranes which were isolated on thin-layer silica plates in air (the same products were obtained in comparable yields by heating the reagents in THF at  $80^\circ$  for 12 hr).



The new compounds were characterized from their  $^{11}\text{B}$  and  $^1\text{H}$  FT NMR, IR, and unit- and high-resolution mass spectra (Tables I-IV), which serve to establish the molecular formulas but do not uniquely define the cage geometries. Although crystal structures of these

materials are not yet available, sufficient information about the structures and reactions of closely related molecules is in hand to permit tentative assignments.

In Figure 1 we indicate a likely reaction pathway with proposed structures of the products. The carborane substrate,  $(CH_3)_4C_4B_8H_8$ , exists in solution as an equilibrium mixture of two isomers,<sup>3</sup> one of which (A) is isolable in the solid state and has been crystallographically characterized.<sup>9</sup> The remaining isomer (B) has not been structurally defined but the structure shown in Figure 1 was recently proposed.<sup>10</sup> Although this geometry is not crucial to the structural assignments of the cobaltocarborane products given below, the inclusion of both  $(CH_3)_4C_4B_8H_8$  isomers in Figure 1 emphasizes the fact that cobalt insertion may well occur in either or both isomeric forms (or in a common intermediate); presently available data do not allow us to identify the specific substrate(s) on which metal attack occurs.

As suggested in Figure 1, the major product 1 [ $(n^5-C_5H_5)Co$    $(CH_3)_4C_4B_7H_7$  (isomer I)] forms via net replacement of one BH unit in  $(CH_3)_4C_4B_8H_8$  with a  $Co(n^5-C_5H_5)$  group. The cage geometry proposed for this species is that of a structurally characterized compound,<sup>11</sup>  $(n^5-C_5H_5)Co(CH_3)_4C_4B_7H_6-OC_2H_5$ , with the ethoxy group replaced by hydrogen. A comparison of FT NMR spectra for the two species is compatible with this assignment; thus, the  $^{11}B$  spectrum<sup>6</sup> of the ethoxy compound exhibits B-H doublets at  $\delta$  11.1, 1.2, -7.9, and -16.8 and a B-OC<sub>2</sub>H<sub>5</sub> singlet at  $\delta$  9.1, with relative areas

1:2:2:1:1, which can be compared with the data for the unsubstituted species in Table I. The proposed structure for I is, moreover, closely related to both the A and B geometries of the carborane precursor,  $(CH_3)_4C_4B_8H_8$ , and can be formally derived from either isomer by replacing B(1)-H with Co( $C_5H_5$ ) and stretching the appropriate framework C-C interactions to produce cage-opening.

Perhaps the strongest support for the assigned structure of I is provided by its synthesis independently from the closo, nido-complex  $[(CH_3)_2C_2B_4H_6]CoH[(CH_3)_2C_2B_3H_5]$  as described below. This alternative route to I is envisioned as occurring via oxidative fusion of the two carborane ligands to generate a  $C_4B_7$  cage into which cobalt is incorporated.

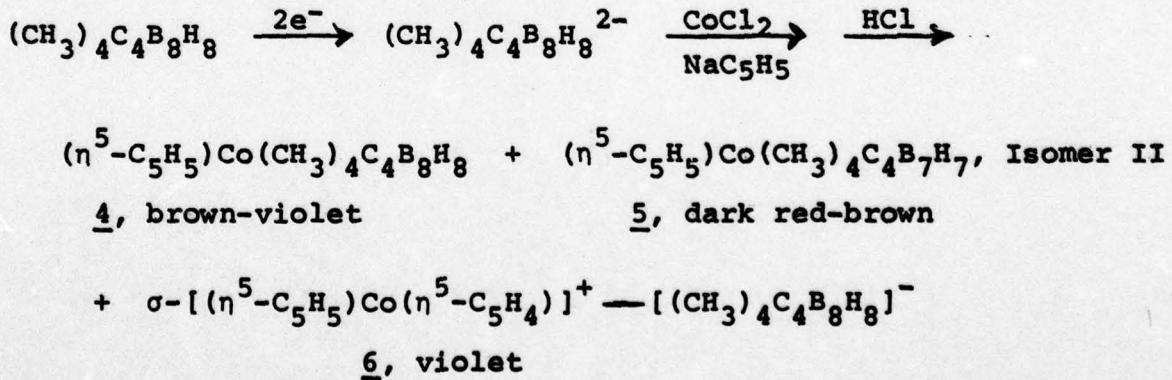
The geometries of the remaining products, isomers I and II of  $(n^5-C_5H_5)Co(CH_3)_4C_4B_6H_6$ , are less certain, but the most likely structures are depicted in Figure 1. Both proposed geometries have mirror symmetry, in agreement with the  $^{11}B$  and  $^1H$  FT NMR data, and both are 11-vertex icosahedral fragments in accordance with the presence of 26 skeletal electrons. Unlike the situation in 12-vertex, 28-electron cages, where distortion from icosahedral symmetry is required by the presence of two "extra" electrons but no single geometry dominates,<sup>11</sup> the obvious choice for an 11-vertex, 26-electron species is an icosahedron with one missing vertex; this is, of course, the structure of the 1,2- and 1,7- $C_2B_9H_{11}^{2-}$  ("dicarbollide") ions<sup>12</sup> which are isoelectronic with the  $CoC_4B_6$  systems.

Several arrangements for the cobalt and carbon atoms in an 11-vertex icosahedral fragment are possible, in addition to those proposed in Figure 2. However, the NMR spectra indicate a mirror plane in each isomer, requiring in turn that the number of carbon atoms on the open face be zero, two, or four; since framework carbons tend to adopt low-coordinate vertices on the open face in open-cage carboranes and metallocarboranes,<sup>13,14</sup> it is likely that both isomers contain  $C_4B$  rather than  $C_2B_3$  or  $B_5$  faces. There are, moreover, readily envisioned pathways for conversion of the  $CoC_4B_7$  to the two proposed  $CoC_4B_6$  species, each of them involving loss of one  $BH$  group and movement of a  $C-CH_3$  unit into the vacated vertex (Figure 1). One other possible structure which contains a  $C_4B$  open face and still retains the mirror plane, has the cobalt in position 10 (numbering as in compound 1). However, since this structure has no carbons adjacent to cobalt and its formation from the  $CoC_4B_7$  species is more difficult to visualize, it appears a less attractive possibility.

Insertion of Cobalt into the  $(CH_3)_4C_4B_8H_8^{2-}$  Ion. The neutral carborane  $(CH_3)_4C_4B_8H_8$  is easily reduced by sodium naphthalide to the dinegative ion as described in an earlier publication.<sup>7</sup> Treatment of this dianion with iron or nickel reagents produces  $MC_4B_7$ ,  $MC_4B_8$ , and  $M_2C_4B_8$  metallocarborane systems, several of which have been crystallographically characterized,<sup>7,8</sup> but the structure of the  $(CH_3)_4C_4B_8H_8^{2-}$  ion itself has never been established. This is a question of some significance since  $(CH_3)_4C_4B_8H_8^{2-}$  is a 12-

vertex, 30-electron arachno species, cage-isoelectronic with  $C_2B_{10}H_{12}^{4-}$  and with the hypothetical ion  $B_{12}H_{12}^{6-}$ ; in principle,<sup>14-16</sup> one would expect such a system to adopt a geometry based on a 14-vertex closo cage (bicapped hexagonal antiprism<sup>17</sup>) with two missing vertices, but structural data have not been available. Unexpectedly, the present investigation provided us with an answer to this question in the form of a  $\sigma$ -bonded derivative of  $(CH_3)_4C_4B_8H_8^{2-}$  which we were able to characterize structurally.

The reaction of  $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$  ion with  $\text{C}_5\text{H}_5^-$  and  $\text{CoCl}_2$  in THF at  $25^\circ$ , followed by acidification with aqueous HCl and isolation of the products on thin-layer silica plates in air, gave small quantities of three compounds. Spectroscopic data on the products



4-6 (Tables I-IV) did not permit structural assignments, but X-ray crystal structure analyses of  $\underline{5}^{18}$  and  $\underline{6}^{10}$  have been obtained. In addition, a recent X-ray study<sup>19</sup> of  $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$ , Isomer I, supplies us with a strong clue to the structure of 4 since

$[(C_6H_5)_2PCH_2]_2Ni$  and  $(C_5H_5)Co$  are each formal 2-electron donors<sup>15,16</sup> to skeletal bonding and the nickel complex is thus an electronic analogue of 4.

As shown in Figure 2, compound 6 is a cobaltocenium-substituted derivative of the  $(CH_3)_4C_4B_8H_9^-$  ion, derived from the  $(CH_3)_4C_4B_8H_8^{2-}$  dianion by addition of  $H^+$  and replacement of  $H\cdot$  with  $(C_5H_5)Co^{III}C$   $(C_5H_4)\cdot^+$  at a boron vertex. A full description of the structure determination, and a discussion of mechanisms of transition metal insertion into the dianion, have been presented elsewhere.<sup>10</sup> For present purposes, it will be noted that 6 contains a bridging  $CH_3CH$  group which spans two mutually nonbonded boron atoms, and that the "extra" hydrogen in the molecule resides on this unique carbon atom. It is assumed that when this proton is absent, as in the  $(CH_3)_4C_4B_8H_8^{2-}$  dianion, the bridging carbon moves fully into the cage framework as shown in the Figure.

On the basis of structural information presently available, we postulate that complexes 4, 5, and 6 form as depicted in Figure 2. Attack of a cobaltocenium radical cation<sup>20</sup> on  $(CH_3)_4C_4B_8H_8^{2-}$  followed by protonation yields 6 as suggested above; however, reaction of the dianion with  $Co(n^5-C_5H_5)^{2+}$  leads to incorporation of the metal into the cage, forming the 13-vertex nido species 4 which can undergo loss of boron to produce the 12-vertex system 5. The proposed structure of 4 has not been established, but is consistent with the NMR data and is supported by two additional observations: it is isostructural with the

known  $\text{NiC}_4\text{B}_8$  system mentioned above, and its conversion to 5 appears straightforward via elimination of a BH group and formation of a carbon-carbon link. From the locations of skeletal carbon atoms in 4, 5, and 6 we infer that 4 and 6 are formed from different isomers of the  $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$  dianion. The presence of dianion isomers is strongly suggested by the plethora of metallocarborane isomers that are obtained on complexation with iron and nickel reagents;<sup>7</sup> mechanistic schemes for the fluxional interconversion of  $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$  isomers have been described in another context.<sup>10</sup>

The established structure of 5 further extends the list of structural types that have been found among tetracarbon species. As shown, the molecule has four- and five-sided open faces which are separated by a  $\text{C}-\text{CH}_3$  group that might be described as bridging three cage atoms; however, this unique carbon atom has no bound hydrogen and hence is not a methylene-type bridge as found in 6. It will be noted that 5 is yet another example of a 12-vertex, 28-electron (nido) framework<sup>11</sup> and constitutes the fifth distinct structural class to be identified among such systems. The X-ray investigation of 5 and its structural and mechanistic implications will be the subject of a future article.<sup>18</sup>

Preparation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{B}_7\text{H}_7$ , Isomer I, from Closo, Nido- $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{CoH}[(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5]$ . The mixed-ligand complex  $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{CoH}[(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5]$ , 7, and some chemistry based on it have been described in an earlier paper,<sup>4</sup> and its structure was

established via an X-ray study of a cobaltocenium-substituted derivative.<sup>22</sup> In the present investigation, 7 was treated with sodium hydride in THF to remove the metal-bound proton<sup>4</sup> and the resulting anion was allowed to react with  $\text{CoCl}_2$  and  $\text{NaC}_5\text{H}_5$ , generating compound 1 (identical to the species obtained from  $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{2-}$  ion) in 14% yield (Figure 3). An alternative procedure employing n-butyllithium as the deprotonating agent and glyme as the solvent, gave the same product.

The formation of 1 from 7 provides additional support for the proposed structure of 1 (vide supra), and also furnishes another example of oxidative ligand fusion.<sup>2</sup> Thus, the merger of formal  $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4^{2-}$  and  $(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5^{2-}$  ligands to form a  $(\text{CH}_3)_2\text{C}_2\text{B}_7\text{H}_7^{2-}$  species from which the neutral monocobalt complex 1 is generated, is analogous to the fusion of two  $(\eta^5\text{C}_5\text{H}_5)\text{CoR}_2\text{C}_2\text{B}_3\text{H}_4^-$  ions to form  $(\eta^5\text{C}_5\text{H}_5)_2\text{Co}_2\text{R}_4\text{C}_4\text{B}_6\text{H}_6$  ( $\text{R} = \text{CH}_3$  or  $\text{H}$ )<sup>5</sup>, or of two  $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4^{2-}$  ligands to produce  $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8^{3,4}$  (other examples have been cited elsewhere<sup>2</sup>).

The mechanism(s) of these fusion processes, including the conversion of 7 to 1, has not been established in detail, but a plausible model is developing from continuing synthetic and structural studies. Thus, a recent crystallographic structure determination of  $[\text{2,3-}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2^{24}$  has revealed that the  $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4^{2-}$  ligands have a mutually staggered conformation which is evidently retained during fusion since the same relationship exists<sup>9</sup> between the  $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$  units in the fused carborane product,  $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ . Further discussion of this question appears elsewhere.<sup>2,24</sup>

#### Thermal Isomerization of $(\eta^5\text{C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ , Isomer I.

In an effort to incorporate an additional metal atom into the framework of 1, that complex was heated with excess  $(\eta^5\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$  in nonane at 140°. However, the only isolable product was

a new isomer of the starting material. The structure of this compound, isomer III (8), has not been assigned, but the  $^{11}\text{B}$  and  $^1\text{H}$  FT NMR spectra indicate the absence of any planes or axes of symmetry. A crystallographic study will clearly be required in this case.

Conclusions

An extraordinary variety of cage structures, many of them without precedent, has been encountered in our exploration of tetracarbon metallocarborane chemistry. It is clear that electronic and steric effects combine to produce a large number of accessible cage geometries. In terms of framework electron count,<sup>15,16,23</sup> most of these systems contain either  $2n + 4$  or  $2n + 6$  electrons (where  $n$  is the number of vertex atoms) and are expected to adopt structures of the nido and arachno types, respectively. The basic problem, as this and earlier work makes clear, is that within these categories so many distinct cage geometries are capable of stable existence. Even in  $(2n + 2)$ -electron systems, where one expects closo polyhedra, open-cage structures that are thermodynamically unfavorable can be stabilized by kinetic effects, as we have previously found in the  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$  system.<sup>8</sup>

Despite the complex stereochemistry exhibited by the tetracarbon systems, the basic patterns of structure and mechanism are gradually emerging as new findings become available. The number of discrete types of polyhedral framework that can be adopted by isolable products is surely limited, and it is reassuring that we have already found duplication in several instances; for example,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_8^7$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_4\text{B}_6\text{H}_{10}$  (isomer VII)<sup>5</sup> exhibit the same cage geometry (though with different heteroatom arrangements),

while other known isopolyhedral pairs consist of the complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_6\text{-OC}_2\text{H}_5$ <sup>11</sup> and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$  (isomer V)<sup>1,5</sup>, and isomers I and V of the  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$  system.<sup>8</sup>

Further work in this area is continuing.

#### Experimental Section

Materials. Tetra-C-methyl-tetracarbadodecaborane(12),  $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ , was prepared from the complex  $[\text{2,3-}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{FeH}_2$  as described elsewhere.<sup>3</sup> All other reagents were commercially obtained reagent grade compounds.

Spectra and Chromotography.  $^{11}\text{B}$  and  $^1\text{H}$  pulse Fourier transform NMR spectra were recorded on a JEOL PS-100P spectrometer interfaced to a JEOL-Texas Instruments EC-100 computer system. Unit resolution mass spectra were obtained on a Hitachi-Perkin Elmer RMU-6E mass spectrometer, and high resolution mass measurements were conducted on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source. All high resolution measurements were performed under chemical ionizing conditions in methane or argon-water. Thin- and preparative-layer chromatography was conducted in air on pre-coated plates of silica-gel F-254 (Brinckman Instruments, Inc.).

Reaction of  $(CH_3)_4C_4B_8H_8$  with  $(\eta^5-C_5H_5)Co(CO)_2$ . The carborane (35 mg, 0.17 mmol) and  $(\eta^5-C_5H_5)Co(CO)_2$  (41 mg, 0.23 mmol) were placed in a quartz reaction vessel and 2 ml of THF was added by distillation. The mixture was irradiated with a Sears 275 watt sun lamp under a nitrogen atmosphere for 96 hr. The reactor was then opened to the atmosphere and stirred for 3 hr after which methylene chloride was added to the black product mixture and the mixture was filtered through silica gel. The resulting filtrate was placed on a silica gel TLC plate (0.5 mm) and was repeatedly developed in hexane. Four significant bands were obtained: band 1, colorless  $(CH_3)_4C_4B_8H_8$ , 9 mg; band 2, yellow  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_6H_6$ , isomer I,  $R_f = 0.32$ , 2 mg; band 3, golden  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_6H_6$ , isomer II,  $R_f = 0.16$ , 2 mg; band 4, red-brown  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_7H_7$ , isomer I,  $R_f = 0.04$ , 4 mg (10% yield based on carborane consumed). The mass spectrum of each metallocarborane product exhibited a strong envelope corresponding to the parent ion, with a profile consistent with the assigned formula. Further characterization was based on  $^{11}B$  and  $^1H$  FT NMR and IR spectra, and on high resolution mass measurements (Tables I-IV).

The products  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_6H_6$  (isomer I) and  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_7H_7$  (isomer I) were also obtained in yields comparable to those given above, by heating an equimolar solution of  $(CH_3)_4C_4B_8H_8$  and  $(\eta^5-C_5H_5)Co(CO)_2$  in n-nonane at  $110^\circ C$  for 2 hr.

Preparation of Metallocarboranes from the  $(CH_3)_4C_4B_8H_8$ <sup>2-</sup>

Ion. To 95 mg (0.49 mmol) of  $(CH_3)_4C_4B_8H_8$  in vacuo at  $-196^\circ$ , were added through a glass frit THF solutions of  $NaC_5H_5$  (4.10 mmol) and sodium naphthalenide (0.95 mmol). The reaction vessel was allowed to come to ambient temperature with stirring, during which the solution color changed from dark green to a clear light pink. To this solution was slowly added from a sidearm addition flask  $CoCl_2$  (351 mg, 2.70 mmol) with constant stirring. The solution color quickly darkened to deep brown with a reddish tint. The solution was stirred for 12 hr after which the reactor was opened to the atmosphere and 0.25 ml of concentrated aqueous HCl in 20 ml of THF was added and the solution stirred for an additional 8 hr. The resulting solution was filtered and solvent removed from the filtrate by distillation in vacuo. The residue was extracted with  $CH_2Cl_2$ , filtered through silica gel, placed on silica gel TLC plates, and developed in benzene, giving three main bands. Band 1, pale yellow, contained  $(CH_3)_4C_4B_8H_8$ , naphthalene, and traces of unidentified metallocarboranes as shown by mass spectroscopic evidence. Band 2 ( $R_f = 0.72$ ) was dark violet and contained two compounds which were subsequently separated by repeated development on a silica gel column in 20% benzene/hexane and characterized as  $(n^5-C_5H_5)Co(CH_3)_4C_4B_7H_7$ , isomer II, 2 mg, and  $(n^5-C_5H_5)Co(CH_3)_4C_4B_8H_8$ , 3 mg. Band 3 (from the original TLC development) was violet  $\sigma-(n^5-C_5H_5)Co(n^5-C_5H_4)-(CH_3)_4C_4B_8H_8$ , 6 mg. The three new compounds

exhibited strong parent envelopes in their mass spectra and were further characterized spectroscopically (Tables I-IV) and by X-ray crystallographic analyses of the first and third products.

Preparation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ , Isomer I, from Closو, Nido- $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4]\text{CoH}[(\text{CH}_3)_2\text{C}_2\text{B}_3\text{H}_5]$ . To a solution of the reactant complex (40 mg, 0.16 mmol) in 2 ml glyme was added 0.17 mmol of  $\eta\text{-C}_4\text{H}_9\text{Li}$  in hexane. The mixture rapidly became dark red with gas evolution; to it were then added 0.65 mmol of  $\text{NaC}_5\text{H}_5$  in 3 ml glyme and 200 mg (1.54 mmol) of solid anhydrous  $\text{CoCl}_2$ . The resulting solution was stirred for 6 hr and then opened to the air. The dark green solution was filtered into 5 ml of THF which had been acidified with 0.25 ml of concentrated aqueous HCl. This solution was stirred, solvent removed, the black-green residue extracted with  $\text{CH}_2\text{Cl}_2$  and filtered through silica gel. The filtrate was placed on a silica gel TLC plate and developed in hexane. Two major bands were obtained, consisting of starting metallocarborane and  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ , isomer I (identical with the product obtained in the reaction of  $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$  with  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}(\text{CO})_2$  together with numerous colored but extremely weak bands. The yield of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$  was 6.5 mg (13% based on the initial quantity of metallocarborane reagent).

The same product was obtained in 14% yield by treatment of the same metallocarborane reagent with NaH in THF followed by addition of excess  $\text{CoCl}_2$  and  $\text{NaC}_5\text{H}_5$  in THF at room temperature.

Thermolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ , Isomer I, with  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ . A 5-mg sample of the metallocarborane and 100 mg of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  were placed in a 5 ml round bottom flask and 1 ml n-nonane was added by distillation in vacuo. The solution was heated under  $\text{N}_2$  at  $110^\circ\text{C}$  for 2.5 hr, after which spot TLC analysis in 20% benzene-hexane revealed the presence of a new red-brown compound together with starting metallocarborane. The reaction mixture was then heated at  $140^\circ\text{C}$  for 18 hr, at which point TLC analysis in 20% benzene-hexane exhibited an intense orange spot ( $R_f \sim 0.2$ ) corresponding to a new compound, but very little of the original metallocarborane. Following removal of volatiles by vacuum distillation, the solid residue was dissolved in  $\text{CH}_2\text{Cl}_2$ , placed on a 0.5 mm silica gel TLC plate, and eluted in 35% benzene/hexane to give one major band characterized as orange  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ , isomer III ( $R_f = 0.40$ , 2.5 mg, 50% yield) plus a small amount (< 1 mg) of the original isomer I.

Acknowledgments. This work was supported by the Office of Naval Research.

References and Notes

- (1) Part 6: J.R. Pipal and R.N. Grimes, Inorg. Chem., in press.
- (2) R.N. Grimes, Acc. Chem. Res., 11, 420 (1978), and references therein.
- (3) W.M. Maxwell, V.R. Miller, and R.N. Grimes, Inorg. Chem., 15, 1343 (1976).
- (4) W.M. Maxwell, V.R. Miller, and R.N. Grimes, J. Am. Chem. Soc., 98, 4818 (1976).
- (5) K-S. Wong, J.R. Bowser, J.R. Pipal, and R.N. Grimes, J. Am. Chem. Soc., 100, 5045 (1978).
- (6) W.M. Maxwell, K-S. Wong, and R.N. Grimes, Inorg. Chem., 16, 3094 (1977).
- (7) W.M. Maxwell, R.F. Bryan, and R.N. Grimes, J. Am. Chem. Soc., 99, 4008 (1977).
- (8) W.M. Maxwell, R. Weiss, E. Sinn, and R.N. Grimes, J. Am. Chem. Soc., 99, 4016 (1977).
- (9) D.P. Freyberg, R. Weiss, E. Sinn, and R.N. Grimes, Inorg. Chem., 16, 1847 (1977).
- (10) R.N. Grimes, J.R. Pipal, and E. Sinn, J. Am. Chem. Soc., in press.
- (11) J.R. Pipal and R.N. Grimes, J. Am. Chem. Soc., 100, 3083 (1978).
- (12) M.F. Hawthorne, D.C. Young, T.D. Andrews, D.V. Howe, R.L. Pilling, A.D. Pitts, M. Reintjes, L.F. Warren, Jr., and P.A. Wegner, J. Am. Chem. Soc., 90, 879 (1968).

(13) In only one nido-carborane or -metallocarborane species known to us,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ , isomer V,<sup>8</sup> is there more than one carbon atom not on an open face.

(14) R.E. Williams, Inorg. Chem., 10, 210 (1971).

(15) K. Wade, Adv. Inorg. Chem. Radiochem., 18, 1 (1976).

(16) R.W. Rudolph, Acc. Chem. Res., 9, 446 (1976).

(17) J.R. Pipal and R.N. Grimes, Inorg. Chem., 17, 6 (1978).

(18) E. Sinn, J.R. Pipal and R.N. Grimes, to be submitted for publication.

(19) E. Sinn and R.N. Grimes, to be submitted for publication.

(20) The formal oxidation state of cobalt is +2 in the starting reagent but +3 in the isolated metallocarborane products; the oxidation of cobalt may take place during workup of the products in air, but probably occurs at least partially at an earlier stage via disproportionation of cobalt species during the reaction (metallic cobalt is frequently obtained<sup>21</sup> in cobaltacarborane syntheses involving  $\text{CoCl}_2$ ).

(21) See, for example, J. Plesek, B. Stibr, and S. Hermanek, Synth. Inorg. Metal-Org. Chem., 3, 291 (1973).

(22) J.R. Pipal, W.M. Maxwell, and R.N. Grimes, Inorg. Chem., 17, 1447 (1978).

(23) D.M.P. Mingos, J. Chem. Soc., Dalton Trans., 602 (1977).

(24) J. R. Pipal and R. N. Grimes, Inorg. Chem., 18, 263 (1979).

Table I. 32.1 - MHz  $^{11}\text{B}$  FT NMR Data<sup>a</sup>

Compounds	$\delta$ , ppm <sup>b</sup> (J, Hz)	Rel Areas
$(\text{C}_5\text{H}_5)_2\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ Isomers Isomer I (1)	16.6(144), 2.0(150) <sup>c,d</sup> , -3.8(140), -8.7(112), -12.9(136), -18.7(144)	1,2,1,1,1,1
Isomer II (5)	23.6(156), 11.7(147), -0.8(136), <sup>c</sup> -2.8(147), -17.6(146), -29.1(146)	1,1,3,1,1
Isomer III (8)	12.8(140) <sup>c</sup> , 11.0(140) <sup>c</sup> , 3.7(137), -8.2(156), -12.7(127)	2,1,2,1,1
$(\text{C}_5\text{H}_5)_2\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$ Isomers Isomer I (2) Isomer II (3)	4.9(156), -9.7(150), -23.4(140) -3.0(160), -10.3(150), -32.1(154)	3,2,1 3,2,1
$(\text{C}_5\text{H}_5)_2\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (4)	12.7(112) <sup>c</sup> , 9.5(146) <sup>c</sup> , 2.3(166) <sup>c</sup> , -7.5(166), -11.5(120), -15.1(136) <sup>c</sup> , -18.5(127) <sup>c</sup>	1,1,1,2,1,1,1
$(\text{C}_5\text{H}_5)_2\text{Co}(\text{C}_5\text{H}_4)-(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (6)	14.9(150), [-6.0, -11.9, -13.4] <sup>e</sup> , -22.2 <sup>f</sup> , -47.2(146)	1, [5], 1, 1

<sup>a</sup>All spectra were obtained in  $\text{CDCl}_3$  solution. <sup>b</sup>Parts per million relative to  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  with positive sign indicating shift to lower field (less shielding). <sup>c</sup>J values estimated from overlapped resonances. <sup>d</sup>Asymmetric peak with shoulder on upfield side.

<sup>e</sup>Chemical shifts obtained from proton-decoupled spectrum;  $J_{\text{H-B}}$  not measurable due to heavy overlap in the undecoupled spectrum.

<sup>f</sup> $\text{B}$ -cobaltocenium resonance.

Table II. 100-MHz  $^1\text{H}$  FT NMR Data<sup>a</sup>

Compound	$\delta$ , ppm <sup>b</sup> (rel area)	Assignment
$(\text{C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_7\text{H}_7$ Isomers		
Isomer I (1)	4.98(5) 2.50(3), 1.92(3), 1.77(6)	$\text{C}_5\text{H}_5$ $\text{CH}_3$
Isomer II (5)	5.15(5) 1.83(3), 1.72(3), 1.36(6) <sup>c</sup>	$\text{C}_5\text{H}_5$ $\text{CH}_3$
Isomer III (8)	5.08(5) 2.30(3), 1.76(3), 1.66(3), 1.61(3)	$\text{C}_5\text{H}_5$ $\text{CH}_3$
$(\text{C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_6\text{H}_6$ Isomers		
Isomer I (2)	5.10(5) 1.82(6), 1.47(6)	$\text{C}_5\text{H}_5$ $\text{CH}_3$
Isomer II (3)	4.81(5) 1.46(6), 1.41(6)	$\text{C}_5\text{H}_5$ $\text{CH}_3$
$(\text{C}_5\text{H}_5)\text{Co}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (4)	5.00(5) 2.64(3), 2.08(3), [1.39, 1.36](6)	$\text{C}_5\text{H}_5$ $\text{CH}_3$
$(\text{C}_5\text{H}_5)\text{Co}(\text{C}_5\text{H}_4)-(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (6)	5.41(5) 5.58(2), 5.30(2) [1.57, 1.55](9), 0.82(3)	$\text{C}_5\text{H}_5$ $\text{C}_5\text{H}_4$ $\text{CH}_3$

<sup>a</sup>All spectra were obtained in  $\text{CDCl}_3$  solution. <sup>b</sup>Parts per million relative to  $(\text{CH}_3)_4\text{Si}$  with positive sign indicating shift to lower field. <sup>c</sup>Area-6  $\text{CH}_3$  peak was just resolvable on  $^{11}\text{B}$ -decoupling at 32.083930 Hz, which produced line narrowing.

Table III. Infrared Absorptions ( $\text{CH}_2\text{Cl}_2$  solution vs.  $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ )

---

1 2928 m, 2853 w, 2523 vs, 1831 w, 1428 m, 1373 m, 1250 w,  
1108 m, 1013 s (doublet), 968 w, sh, 938 w, 863 w, 828 s.

2 2950 w, sh, 2920 m, 2855 m, sh, 2530 s, 1450 m, 1420 w, 1390 w,  
1375 w, 1245 w, broad, 1035 w, 1008 w (doublet), 960 w, 928 m,  
905 w, 847 w, 838 m, 739 w.

3 2940 m, 2870 w, 2580 s, 2520 m, sh, 1422 m, broad, 1380 w (doublet),  
1248 w, broad, 1170 w, 1105 w, 1080 w, 1065 w, 1020 w, 990 w,  
935 w, 865 w, 820 s.

4 2930 s, 2860 m, 2540 vs, 2440 m, sh, 1725 w, broad, 1430 m, broad,  
1375 w, 1250 m, broad, 1120 w, 1070 m, 1020 w, 995 w, 902 m, broad,  
838 s, 690 m, broad.

5 2955 w, sh, 2925 m, 2860 w, 2525 s, 1430 m, broad,  
1373 w, 1250 m, broad, 1005 w, 833 m.

6 2950 w, 2930 m, 2860 m, 2540 s, 1725 w, br, 1430 m, broad  
1250 m, 1005 m, 895 w, 845 w, 700 s.

Table IV. High Resolution Mass Measurements<sup>a</sup>

Compound	Formula	Calcd	Mass
			Obsd
<u>1</u> <sup>b</sup>	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_7^{1}\text{H}_{24}^{+}$	316.1862	316.1866
	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_7^{1}\text{H}_{25}^{+}$	317.1940	317.1923
<u>2</u>	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_6^{1}\text{H}_{23}^{+c}$	304.1690	304.1721
	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_5^{10}\text{B}_1^{1}\text{H}_{23}^{+c}$	303.1725	303.1731
<u>3</u>	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_6^{1}\text{H}_{24}^{+}$	305.1769	305.1769
<u>4</u>	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_8^{1}\text{H}_{26}^{+}$	329.2111	329.2096
<u>5</u>	$^{59}\text{Co}^{12}\text{C}_{13}^{11}\text{B}_7^{1}\text{H}_{25}^{+}$	317.1940	317.1942
<u>6</u>	$^{59}\text{Co}^{12}\text{C}_{18}^{11}\text{B}_8^{1}\text{H}_{30}^{+}$	393.2424	393.2424

<sup>a</sup>Mass of P + 1 ion (protonated parent ion) obtained in methane under chemical ionizing conditions. <sup>b</sup>Spectrum obtained in

argon-water. <sup>c</sup>Parent (P) ions.

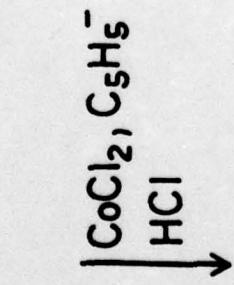
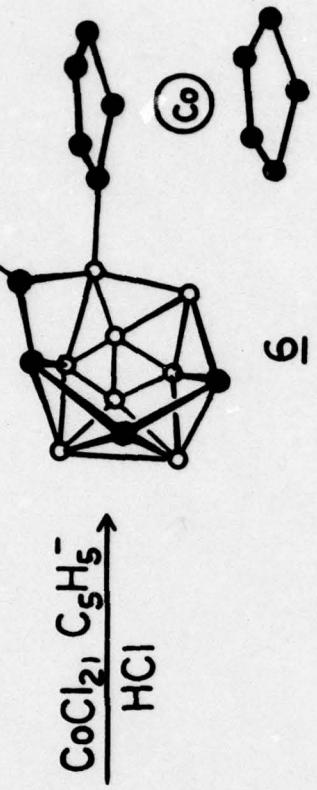
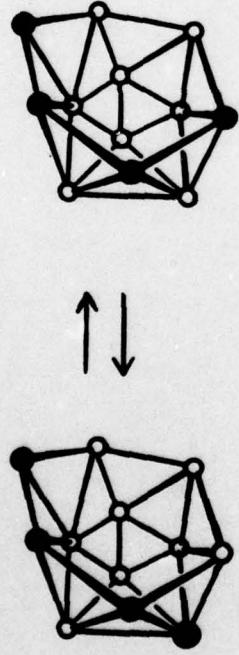
Figure Captions

**Figure 1.** Scheme for the preparation of 11- and 12-vertex nido-cobaltacarboranes from neutral  $(CH_3)_4C_4B_8H_8$ . The structure of  $(CH_3)_4C_4B_8H_8$  (isomer A) is established;<sup>9</sup> those of isomer B,  $(\eta^5-C_5H_5)Co\bigcirc (CH_3)_4C_4B_7H_7$  (isomer I), and  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_6H_6$  (isomers I and II) are proposed from NMR and other evidence. Both isomers of the  $CoC_4B_6$  system have mirror symmetry.

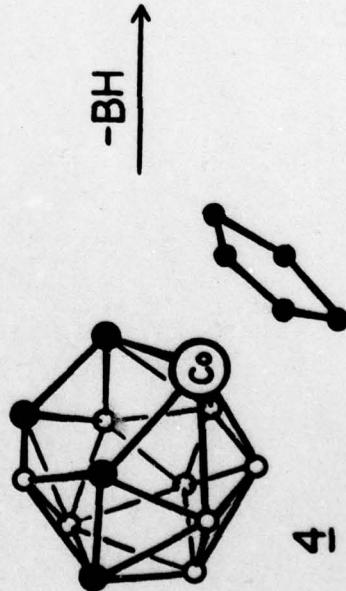
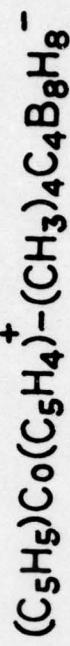
**Figure 2.** Scheme for the preparation of  $\sigma-[(\eta^5-C_5H_5)Co(\eta^5-C_5H_4)^+-(CH_3)_4C_4B_8H_8^-$  (6),  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_8H_8$  (4), and  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_7H_7$  (5) from the  $(CH_3)_4C_4B_8H_8^{2-}$  dianion. The structures of 5 and 6 are known from X-ray studies,<sup>18,10</sup> and that of 4 is based on the established structure<sup>19</sup> of  $[(C_6H_5)_2PCH_2]_2Ni(CH_3)_4C_4B_8H_8$ . The proposed interconversion of  $(CH_3)_4C_4B_8H_8^{2-}$  isomers shown here is described in detail elsewhere.<sup>10</sup>

**Figure 3.** Alternate synthesis of  $(\eta^5-C_5H_5)Co(CH_3)_4C_4B_7H_7$  (isomer I) from closo, nido- $[(CH_3)_2C_2B_4H_4]CoH[(CH_3)_2C_2B_3H_5]$  (7). The conversion probably involves oxidative fusion of the  $(CH_3)_2C_2B_4H_4^{2-}$  and  $(CH_3)_2C_2B_3H_5^{2-}$  ligands in 7 to form  $(CH_3)_4C_4B_7H_7$ , with subsequent addition of cyclopentadienylcobalt to the latter species.

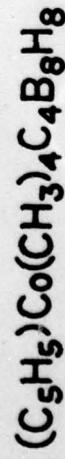
—  $(CH_3)_4C_4B_8H_8^{2-}$  ISOMERS —



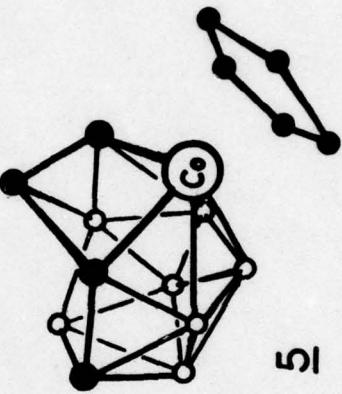
6



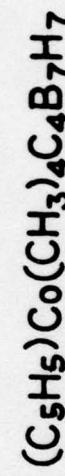
4



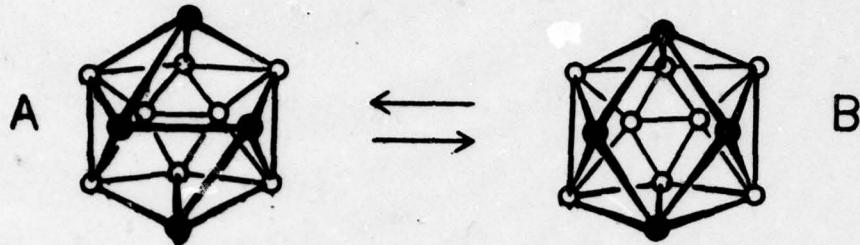
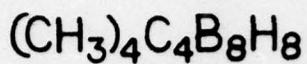
ISOMER II



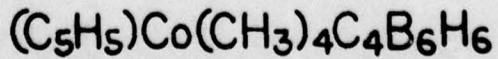
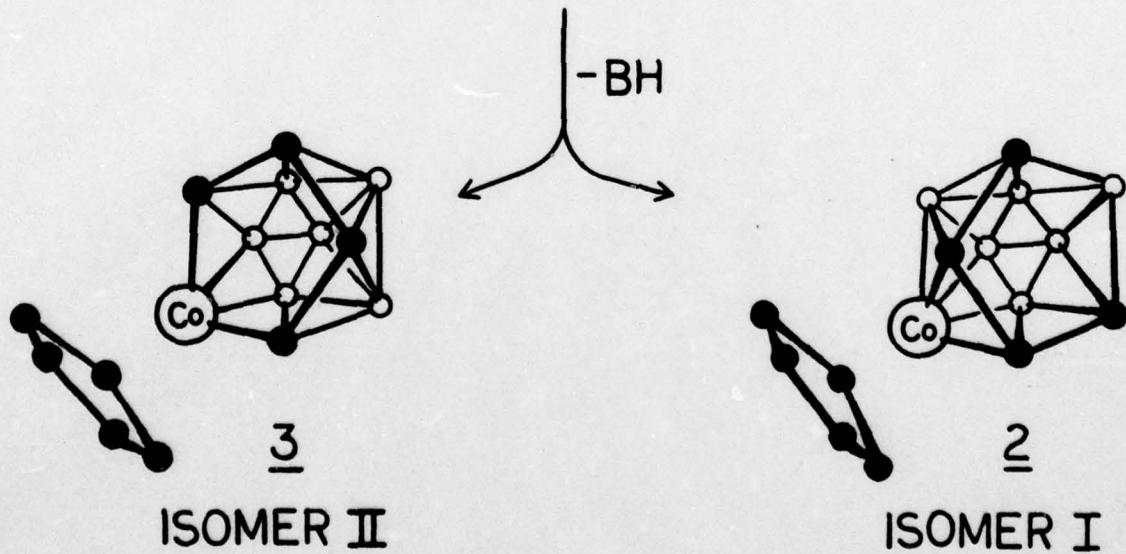
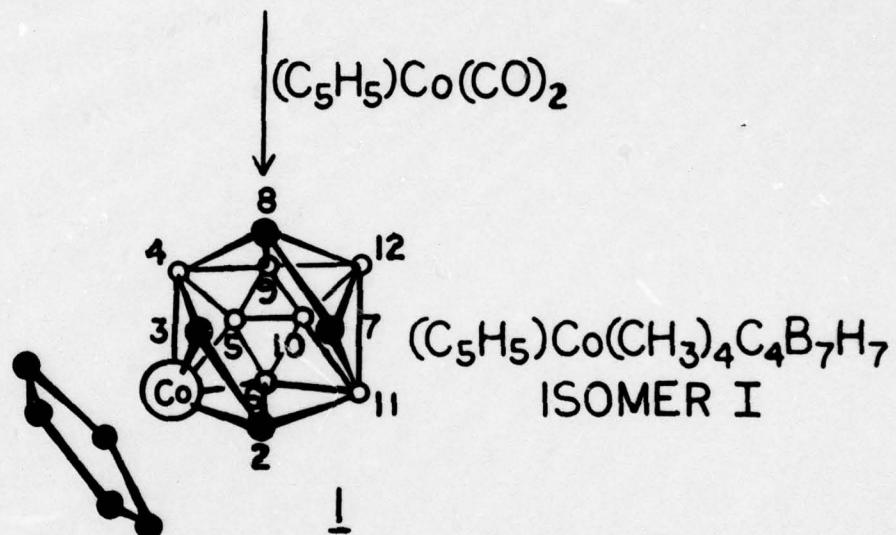
5

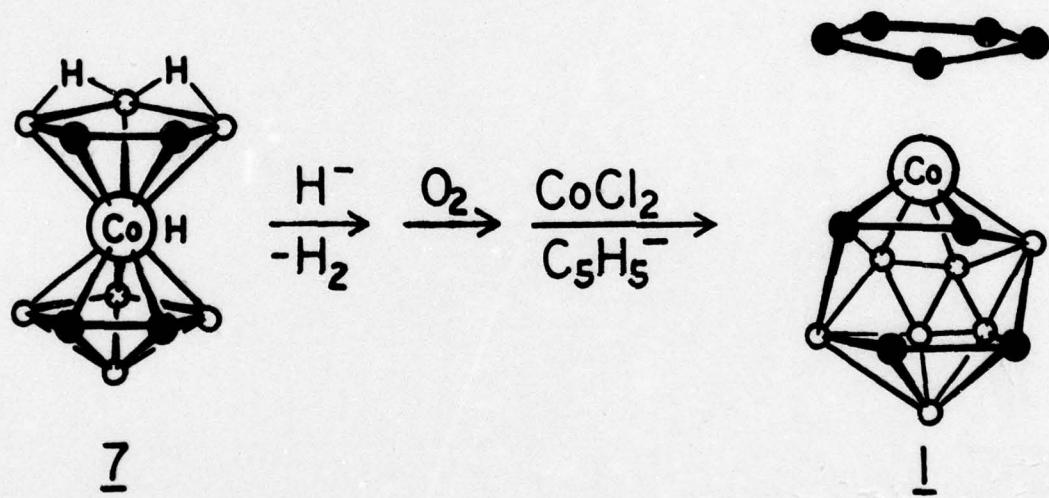


ISOMER II



○ BH  
● CH,  
CCH<sub>3</sub>





## UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 28	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Tetracarbon Metallocarboranes. 7. Cobalt Systems Derived from $(CH_3)_4C_1B_8H_8$ . Synthesis and Inter-Conversion of 11-, 12-, and 13-Vertex Nido Cages		5. TYPE OF REPORT & PERIOD COVERED Interim
7. AUTHOR(s) William M. Maxwell and Russell N. Grimes		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Virginia Department of Chemistry Charlottesville, Virginia 22901		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-569
11. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Branch, Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE April, 1979
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 26
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		15. SECURITY CLASS. (of this report) Unclassified
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Metallocarboranes Cobaltacarboranes Dimetallocarboranes Nido-metallocarboranes Polyhedral rearrangement Tetracarbon metallocarboranes		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See page 1		

**TECHNICAL REPORT DISTRIBUTION LIST, GEN**

<u>No.</u>	<u>Copies</u>	<u>No.</u>	<u>Copies</u>
Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1	U.S. Army Research Office P.O. Box 1211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Weapons Center China Lake, California 93555 Attn: Dr. A. B. Amster Chemistry Division	1
ONR Area Office One Hallidie Plaza, Suite 601 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Naval Civil Engineering Laboratory Port Hueneme, California 93401 Attn: Dr. R. W. Drisko	1
ONR Branch Office Building 114, Section D 666 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Professor K. E. Wohler Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (R, E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1	Naval Ship Research and Development Center Annapolis, Maryland 21401 Attn: Dr. G. Bosmajian Applied Chemistry Division 1	1
		Naval Ocean Systems Center San Diego, California 91232 Attn: Dr. S. Yamamoto, Marine Sciences Division	1

TECHNICAL REPORT DISTRIBUTION LIST, 053

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. K. N. Grimes University of Virginia Department of Chemistry Charlottesville, Virginia 22901	1	Dr. M. H. Chisholm Department of Chemistry Indiana University Bloomington, Indiana 47401	1
Dr. M. Tsutsui Texas A&M University Department of Chemistry College Station, Texas 77843	1	Dr. B. Foxman Brandeis University Department of Chemistry Waltham, Massachusetts 02154	1
Dr. M. F. Hawthorne University of California Department of Chemistry Los Angeles, California 90024	1	Dr. T. Marks Northwestern University Department of Chemistry Evanston, Illinois 60201	1
Dr. D. B. Brown University of Vermont Department of Chemistry Burlington, Vermont 05401	1	Dr. G. Geoffrey Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1
Dr. W. B. Fox Naval Research Laboratory Chemistry Division Code 6130 Washington, D.C. 20375	1	Dr. J. Zuckerman University of Oklahoma Department of Chemistry Norman, Oklahoma 73019	1
Dr. J. Adcock University of Tennessee Department of Chemistry Knoxville, Tennessee 39716	1	Professor O. T. Beachley Department of Chemistry State University of New York Buffalo, New York 14214	1
Dr. W. Hatfield University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514	1	Professor P. S. Skell Department of Chemistry The Pennsylvania State University University Park, Pennsylvania 16802	1
Dr. D. Seyferth Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1	Professor K. M. Nicholas Department of Chemistry Boston College Chestnut Hill, Massachusetts 02167	1